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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US00/09796 <b>(22) International Filing Date:</b> 12 April 2000 (12.04.00)  <b>(30) Priority Data:</b> 60/128,902                      12 April 1999 (12.04.99)                      US  <b>(71) Applicant (for all designated States except US):</b> ARIZONA BOARD OF REGENTS [US/US]; Arizona State University, Tempe, AZ 85287-6006 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> ANGELL, Charles, A. [US/US]; 2122 S. Paseo Loma, Mesa, AZ 85202 (US). VELLIKOV, Vesselin [BG/US]; 4533 S. Mill Avenue, Tempe, AZ 85282 (US).  <b>(74) Agents:</b> SORELL, Louis, S. et al.; Baker & Botts LLP, 30 Rockefeller Plaza, New York, NY 10112-0228 (US).		<b>(81) Designated States:</b> CA, JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> TWO-PHASE REFRIGERATION FLUID FOR AN ABSORPTION REFRIGERATION APPARATUS AND A METHOD OF PREVENTING CORROSION  <b>(57) Abstract</b>  A novel two-phase refrigeration fluid for absorption refrigeration comprises a first phase that is an aqueous solution of lithium halide, the second phase is an aqueous solution of a fluorinated salt of lithium. The refrigeration fluid of the present invention offers high boiling temperatures and corrosion protection.		

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## TWO-PHASE REFRIGERATION FLUID FOR AN ABSORPTION REFRIGERATION APPARATUS AND A METHOD OF PREVENTING CORROSION

### SPECIFICATION

#### 5                    BACKGROUND OF INVENTION

                  This invention relates to the field of absorption refrigeration. Specifically, the invention provides a novel refrigeration fluid and a related method of preventing corrosion of internal parts in an absorption refrigeration apparatus.

                  Modern absorption refrigeration is based on a cooling effect obtained  
10   by connecting two vessels containing liquids with different vapor pressures. The cooling effect is produced in the vessel containing the liquid with higher vapor pressure when the vapors are drawn to the vessel containing the liquid with lower vapor pressure. Typically, an aqueous solution of lithium halide is used as the liquid with lower vapor pressure and water is used as the liquid with higher vapor pressure.  
15   The liquid with lower vapor pressure is called the refrigeration fluid. An aqueous solution of lithium bromide is the typical refrigeration fluid used in absorption refrigeration.

                  Figure 1 illustrates the operation of a typical absorption refrigeration cycle. An evaporator 1 contains a liquid with higher vapor pressure, usually water,  
20   and is connected to an absorber 2, which contains a refrigeration fluid, usually a solution of lithium bromide. The refrigeration fluid is sprayed in the absorber 2. Because of the difference in vapor pressures, the water vapors from the evaporator 1 are drawn into the absorber, producing a cooling effect in the evaporator. The refrigeration fluid is then transferred to a generator 3. In the generator, the  
25   refrigeration fluid is boiled to produce water vapors and a more concentrated solution of the refrigeration fluid. The concentrated refrigeration fluid is continuously returned from the generator 3 to the absorber 2 by spraying. The water vapors produced in the

generator 3 are condensed in a condenser 4. The condensed water is then transferred to the evaporator 1, completing the absorption refrigeration cycle.

The cooling effect produced in absorption refrigeration may be magnified by an increase in the vapor pressure gradient between the absorber 2 and the evaporator 1. In turn, the vapor pressure gradient may be increased by an increase in the boiling temperature of the refrigeration fluid in the generator 3. The higher boiling temperature decreases the vapor pressure of the refrigeration fluid, resulting in a larger vapor pressure gradient and a larger cooling effect in the evaporator. In effect, the absorption refrigeration is based on utilizing the heat supplied to the generator 3 to cool the evaporator 1.

It is known that stagewise utilization of heat improves the efficiency of absorption refrigeration. The process for stagewise utilization of heat is known as "double effect" and "triple effect" absorption refrigeration, depending on the number of heat utilization stages.

At present, the use of "double effect" and "triple effect" absorption refrigeration is not feasible due to insufficiently high boiling temperatures of conventional lithium bromide refrigeration fluids. So far, the efforts to produce higher boiling and practical refrigeration fluids have not been successful. The boiling temperatures are limited by chemical stability of refrigeration fluids and the ability of the internal parts of refrigeration equipment to withstand corrosion. For example, it is known that the addition of zinc bromide to the lithium bromide refrigeration fluid significantly increases the boiling temperature. The resulting solution of tetrabromozincate is also chemically stable in the range of temperatures used in absorption refrigeration. However, the lithium tetrabromozincate is corrosive to the internal parts of refrigeration equipment.

Therefore, there is a need for an absorption refrigeration fluid which is both stable to high temperatures and not corrosive.

It is an object of the present invention to provide a refrigeration fluid for an absorption refrigeration apparatus which is chemically stable within the range of temperatures used in absorption refrigeration and not corrosive to the internal parts and piping of an absorption refrigeration apparatus.

It is also an object of the present invention to provide a method of protecting absorption refrigeration equipment from corrosion.

### SUMMARY OF THE INVENTION

The present invention fulfills this need by providing a refrigeration fluid which is a two-phase liquid, wherein the first phase is an aqueous solution of lithium halide and the second phase is an aqueous solution of a fluorinated salt of lithium.

The present invention also provides an absorption refrigeration apparatus which includes an evaporator, an absorber, a generator, a condenser and a refrigeration fluid which is a two-phase liquid, wherein the first phase is an aqueous solution of lithium halide, the second phase is an aqueous solution of a fluorinated salt of lithium.

In addition, the present invention also provides a method for protecting internal parts of an absorption refrigeration apparatus by using the two-phase refrigeration fluid of the present invention.

### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a general scheme of the absorption refrigeration cycle.

Figure 2 shows a phase diagram for a two-component system of lithium bis (trifluoro methane sulfonyl) imide ("LiTFMSI") and water.

Figure 3 shows a phase diagram for a two-component system of lithium bromide and water.

Figure 4 shows a plot of boiling temperatures and glass transition temperatures for aqueous solutions of LiBr and LiTFMSI as a function of salt concentrations.

### DETAILED DESCRIPTION OF THE INVENTION

As discussed above, the desired increase in the boiling temperatures of refrigeration fluids for absorption refrigeration is limited by the chemical stability and corrosive nature of known refrigeration fluids. However, in this invention, a two-

phase liquid wherein the first phase is an aqueous solution of lithium halide and the second phase is an aqueous solution of a fluorinated salt of lithium is an excellent refrigeration fluid for absorption refrigeration which is both stable in the temperature range used in absorption refrigeration and minimally corrosive to the internal parts of an absorption refrigeration apparatus.

Without wishing to be bound to any one theory, this invention is based on a completely unexpected phenomena of immiscibility of aqueous solutions of fluorinated salts of lithium with aqueous solutions of lithium halides in a wide range of concentrations. Aqueous solutions are normally expected to mix and form a single continuous phase. However, for example, when the aqueous solution of lithium bis(trifluoro methane sulfonyl) imide was added to the aqueous solution of lithium bromide, the resulting liquid unexpectedly contained two aqueous phases.

The relevance of this phenomena to absorption refrigeration lies in the recognition that the fluorinated phase has lower surface tension than the lithium halide phase. It is well known that fluorinated groups are hydrophobic and that compounds containing fluorinated groups are often used as surfactants because of their lower surface tension. Indeed, when a metal or glass object was inserted into a two-phase liquid according to the present invention, for example, into the lithium bromide/lithium bis(trifluoro methane sulfonyl) imide solution, the fluorinated phase was qualitatively observed to exhibit a lower contact angle, and therefore, the lower surface tension of the fluorinated phase. It has also been shown by others that a dissolution of lithium bis(trifluoro methane sulfonyl) imide in water, in contrast to lithium halide salts, leads to a significant decrease in the surface tension of the resulting aqueous solution from 70 dyn/cm to about 35 dn/cm, see G. Perron et al., Can. J. Chem., 75, 1608-1614 (1997), incorporated herein by reference.

Further, when a two-phase liquid is placed in a vessel, the phase with lower surface tension will adhere to the surfaces of the vessel. Therefore, when the refrigeration fluid of the present invention is used in a refrigeration apparatus, the fluorinated phase positions itself between the internal surfaces of the apparatus and the lithium halide phase. As a result, it is believed that the fluorinated phase prevents contact between the internal surfaces and the lithium halide phase, protecting the

surfaces and minimizing corrosion. In addition, the fluorinated phase is likely to stabilize a thin film of  $\text{NiF}_2$  or  $\text{CuF}_2$  on nickel-containing copper materials, commonly used for piping in absorption refrigeration.

The fluorinated phase of the refrigeration fluid of the present invention includes a fluorinated salt of lithium, for example, a fluorinated salt of the formulas  $\text{LiC}_n\text{H}_{2n+1}\text{SO}_2\text{N}$ ,  $\text{Li}(\text{C}_n\text{H}_{2n+1}\text{SO}_2)_2\text{N}$  or  $\text{LiC}_n\text{H}_{2n+1}\text{PO}_2$ , wherein  $n$  is from 1 to 3. Preferably, the aqueous solutions of lithium bis (trifluoro methane sulfonyl) imide ("LiTFMSI"), lithium bis(perfluoroethanesulfonyl)imide ("LiBETI"),  $\text{Li}(\text{CF}_3)_2\text{PO}_2$ ,  $\text{Li}(\text{C}_3\text{F}_7\text{SO}_2)_2\text{N}$ ,  $\text{Li}(\text{C}_2\text{F}_5)_2\text{PO}_2$ , as well as their mixtures, are used in the preparation of the fluorinated phase. In addition, the aqueous solutions of  $\text{LiSbF}_6$ ,  $\text{LiAsF}_6$  and lithium perfluoro benzene sulfonate, as well as their mixtures, may also be used in the preparation of the fluorinated phase.

The lithium halide phase of the refrigeration fluid of the present invention preferably includes either lithium bromide or lithium chloride. In a particularly preferred embodiment, the first phase is an aqueous solution of lithium bromide and the second phase is an aqueous solution of lithium bis (trifluoro methane sulfonyl) imide (LiTFMSI).

To increase the boiling temperature of the refrigeration fluid of the present invention, a suitable inorganic salt additive, for example, zinc bromide ( $\text{ZnBr}_2$ ), may be utilized. The addition of zinc bromide produces tetrabromozincate in the lithium bromide phase, resulting in a stable, high-temperature boiling liquid. In contrast to the presently known use of tetrabromozincate in absorption refrigeration, the fluorinated phase will prevent contact between the tetrabromozincate-containing phase and the internal surfaces of the refrigeration apparatus, thereby minimizing corrosion. At the same time, the boiling temperature of the refrigeration fluid will increase, while heat transfer from the internal surfaces to the lithium bromide phase will not be affected by the presence of the fluorinated phase because both phases are aqueous. Thus both prevention of corrosion and higher boiling temperatures are achieved by utilizing the refrigeration fluid of the present invention.

Other suitable additives may also be used in the refrigeration fluid of the present invention, for example, lithium trifluoromethane sulfonate and lithium fluoride.

A solution of a lithium halide, for example, lithium bromide, may represent a major portion of the refrigeration fluid of the present invention. Specifically, lithium halide may represent over 90% by weight with respect to the total weight of salt in the refrigeration fluid of the present invention. Preferably, lithium halide represents over 95% by weight with respect to the total weight of salts in the refrigeration fluid; most preferably, lithium halide represents 99% by weight. It is sufficient to provide a small layer of fluorinated protection between the lithium halide (e.g., lithium bromide) phase and the internal parts of the refrigeration apparatus. Preferably, the fluorinated salt is present in an amount of up to 5% by weight with respect to the total salt content. Most preferably, the fluorinated salt is present in an amount of 1% by weight with respect to the total salt content.

The vapor pressure of a liquid, and thus its boiling point, is proportional to the chemical potential of the liquid. Any two-phase system exists at an equilibrium where chemical potentials of the phases are identical. Therefore, the boiling point of a two-phase system is likely to be intermediate between the boiling points of each separate phase at the corresponding salt concentrations.

When two immiscible aqueous phases are mixed, water will redistribute itself to equalize the chemical potentials of the phases. The proper functioning of the refrigeration fluid requires similar boiling points for each liquid phase in the two-phase refrigeration fluid to prevent an excessive redistribution of water. Therefore, to evaluate the behavior of the two-phase refrigeration fluid of the present invention in the absorption refrigeration cycle, it is necessary to compare the boiling points of the lithium halide phase and the fluorinated phase at various salt concentrations.

The LiBr/LiTFMSI system was chosen as an example. The boiling behavior for the LiBr/ LiTFMSI two-phase system may be estimated from the plots for boiling points of the individual LiBr/water and LiTFMSI/water systems at different salt concentrations, as shown in Figures 2 and 3, excerpted from G. Perron et al., Can. J. Chem., 75, 1608-1614 (1997) and A. Sivaraman, H. Senapati, C.A. Angell,



J. Phys. Chem., B, 103(20), 4159 (1999), which are incorporated herein by reference. Figure 4 combines the data shown in Figures 2 and 3 and demonstrates that boiling behaviors of LiBr and LiTFMSI phases are very similar. The closeness of boiling points for LiBr and LiTFMSI solutions at identical salt concentrations indicates that mixing of the phases is unlikely to result in an unreasonably large redistribution of water. It should be noted that suitable additives may be used to modify the refrigeration fluid in order to prevent excessive redistribution of water. These additives may include, for example, lithium fluoride, lithium trifluoromethane sulfonate, as well as any of the fluorinated salts shown above.

The present invention is further demonstrated by reference to the examples that follow. The examples are given for the purpose of illustration, and are not meant to be limiting in any way.

#### Preparation of the refrigeration fluid

##### Example 1.

Approximately 8.61 g of LiTFMSI was dissolved in 1.39 ml of distilled water with stirring to produce an aqueous solution of LiTFMSI. Similarly, 6.52 g of LiBr were dissolved in 3.48 ml of water to produce an aqueous solution of lithium bromide. 9 g of the LiBr solution was added to 2.5 g of the LiTFMSI solution with stirring. The resulting liquid contained two aqueous phases. The two-phase liquid was heated in an Erlenmeyer flask until the boiling has commenced in the flask. On visual observation, the phase separation and the volumes of the LiBr and LiTFMSI phases remained unaffected. The boiling commenced in the LiTFMSI phase, which then initiated the boiling of the LiBr phase.

##### Example 2.

28 mole % solutions of LiTFMSI and LiBr were prepared by using the appropriate amounts of corresponding salts and distilled water. 5.4 g of the LiTFMSI solution were added to 19.5 g of the LiBr solution resulting in a molar ratio of LiTFMSI to LiBr of 1:9. After stirring and heating to below the boiling point, the solution

remained separated into two phases.

### Example 3

0.11 g of the LiTFMSI solution obtained in Example 2 were added to 5 g of the LiBr solution, resulting in a molar ratio of LiTFMSI to LiBr of 0.7 : 99.3. After  
5 vigorous stirring and heating the two aqueous phases are still immiscible.

### Example 4.

16.7 mole % aqueous solutions of lithium bis(perflouroethanesulfonyl)imide ("LiBETI") and LiBr were prepared by adding the salts to the appropriate amounts of distilled water. Upon dissolution, 8.32 g of the LiBr  
10 solution was added to a vial containing 5.71 g of the BETI solution, resulting in a ratio of LiBETI to LiBr of 1:4 . The resulting liquid contained two aqueous phases. The two-phase liquid was heated in an Erlenmeyer flask. On visual observation, the phase separation and the volumes of the LiBr and LiBETI phases remained unaffected by heating.

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### Detection of immiscibility limits (plait point)

### Example 5

The solution from example 2 was subjected to stepwise dilution by adding about 2.5 g of water at a time. As the overall molar concentration of the solution decreased to 22.6 %, 18.9 %, and 16.3 %, the two phases remained separated and  
20 unaffected by stirring and heating. The added water was absorbed predominantly by the LiBr phase. At an overall composition of 13.9 mole %, upon heating and vigorous stirring, the cloudiness disappeared at about 82-86°C and the two phases mixed together. Thus, 13.9 mole% is the plait point for this temperature. Upon cooling, the solution became turbid and the two phases separated at room temperature.

## Example 6

The solution obtained in Example 3 was subjected to dilution with 0.5 g of water at a time to determine the plait point for the two-phase liquid with low relative concentration of LiTFMSI salt. At an overall molar concentrations of 23.0 % and 19.6 %  
5 %, the two aqueous phases are immiscible at all temperatures up to just below the boiling point. At 17.2 mole % of salt, upon vigorous stirring, the solution clears up at room temperature, indicating that the plait point at room temperature lies between 19.6 and 17.2 mole %.

Hypothetical Example 1A.

10 Approximately 70 g of lithium perfluoro benzene sulfonate was dissolved in 50 ml of distilled water with intensive stirring to produce approximately 120 g of the fluorinated phase. Separately, 50 g of lithium bromide was dissolved in 50 ml of water to produce 100 g of stock LiBr solution. 20 g of the resulting solution of LiBr was weighed and transferred into a 100 ml round-bottom flask and charged with mechanical  
15 stirrer. After the stirring was started, approximately 2 g of the lithium perfluoro benzene sulfonate solution was added to the flask. Stirring continued for approximately 10 min. The solution was allowed to settle. After settling, approximately 1 g of  $\text{ZnBr}_2$  and 2 g of LiF were added to the flask. The flask was charged with a reflux condenser and the liquid was heated to reflux. On observation, both lithium halide and the fluorinated phase  
20 are expected to boil simultaneously. The resulting two-phase liquid can be used as a refrigeration fluid.

Hypothetical Example 1B.

The refrigeration fluid was prepared using  $\text{LiSbF}_6$  and LiCl using the procedure shown in hypothetical Example 1A.

25

Hypothetical Example 1C.

The refrigeration fluid was prepared using  $\text{Li}(\text{C}_3\text{F}_7\text{SO}_2)_2\text{N}$  and LiBr using the procedure shown in hypothetical Example 1A.

The above embodiments have shown various aspects of the present invention. Other variations be evident to those skilled in the art and such modifications are intended to be within the scope of the invention as defined by the appended claims.

CLAIMS

1. A refrigeration fluid comprising a two-phase liquid, wherein the first phase comprises an aqueous solution of lithium halide, and the second phase comprises an aqueous solution of a fluorinated salt of lithium.
- 5 2. The refrigeration fluid according to claim 1, wherein the first phase comprises an aqueous solution of lithium bromide.
3. The refrigeration fluid according to claim 1, wherein the fluorinated salt of lithium is selected from the group consisting of lithium bis (trifluoro methane sulfonyl) imide, lithium bis(perfluoroethanesulfonyl)imide,  $\text{LiSbF}_6$ ,  $\text{LiAsF}_6$ ,  
10  $\text{Li}(\text{CF}_3)_2\text{PO}_2$ ,  $\text{Li}(\text{C}_3\text{F}_7\text{SO}_2)_2\text{N}$ ,  $\text{Li}(\text{C}_2\text{F}_5)_2\text{PO}_2$  and lithium perfluoro benzene sulfonate.
4. The refrigeration fluid according to claim 3, wherein the fluorinated salt of lithium is lithium bis (trifluoro methane sulfonyl) imide.
5. The refrigeration fluid according to claim 1, wherein the first phase represents a major portion of the refrigeration fluid.
- 15 6. The refrigeration fluid according to Claim 1, further comprising  $\text{ZnBr}_2$ .
7. An absorption refrigeration apparatus comprising
  - (a) an evaporator for evaporating water;
  - (b) an absorber wherein water is absorbed into a refrigeration fluid comprising a two-phase liquid wherein the first phase comprises an aqueous solution  
20 of lithium halide and the second phase comprises an aqueous solution of a fluorinated salt of lithium;
  - (c) a generator connected to the absorber, wherein the refrigeration fluid is transferred from the absorber, and is heated to release water vapor; and
  - (d) a condenser wherein water is condensed and transferred to the  
25 evaporator.

8. The refrigeration apparatus according to claim 7, wherein the first phase comprises an aqueous solution of lithium bromide.
9. The refrigeration apparatus according to claim 7, wherein the fluorinated salt of lithium is selected from the group consisting of lithium bis (trifluoro methane sulfonyl) imide, lithium bis(perflouroethanesulfonyl)imide,  $\text{LiSbF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{Li}(\text{CF}_3)_2\text{PO}_2$ ,  $\text{Li}(\text{C}_3\text{F}_7\text{SO}_2)_2\text{N}$ ,  $\text{Li}(\text{C}_2\text{F}_5)_2\text{PO}_2$  and lithium perfluoro benzene sulfonate.
10. The refrigeration apparatus according to claim 9, wherein the fluorinated salt of lithium is lithium bis (trifluoro methane sulfonyl) imide.
11. The refrigeration apparatus according to claim 7, wherein the first phase represents a major portion of the refrigeration fluid.
12. The refrigeration apparatus according to Claim 7, wherein the refrigeration fluid further comprises  $\text{ZnBr}_2$ .
13. A method of protecting internal parts of an absorption refrigeration apparatus comprising providing a refrigeration fluid which comprises a two-phase liquid, wherein the first phase has a higher surface tension than the second phase, thereby the second phase adheres to the internal parts of the refrigeration apparatus and thereby the second phase is positioned between the internal parts of the refrigeration apparatus and the first phase.
14. A method of protecting internal parts of an absorption refrigeration apparatus comprising providing a refrigeration fluid which comprises a two-phase liquid wherein the first phase comprises an aqueous solution of lithium halide, and the second phase comprises an aqueous solution of a fluorinated salt of lithium, and the second phase is positioned between the internal parts of the refrigeration apparatus and the first phase.

15. The method according to claim 14, wherein the first phase comprises an aqueous solution of lithium bromide.

16. The method according to claim 14, wherein the fluorinated salt of lithium is selected from the group consisting of lithium bis (trifluoro methane sulfonyl) imide, lithium bis(perfluoroethanesulfonyl)imide,  $\text{LiSbF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{Li}(\text{CF}_3)_2\text{PO}_2$ ,  $\text{Li}(\text{C}_3\text{F}_7\text{SO}_2)_2\text{N}$ ,  $\text{Li}(\text{C}_2\text{F}_5)_2\text{PO}_2$  and lithium perfluoro benzene sulfonate.

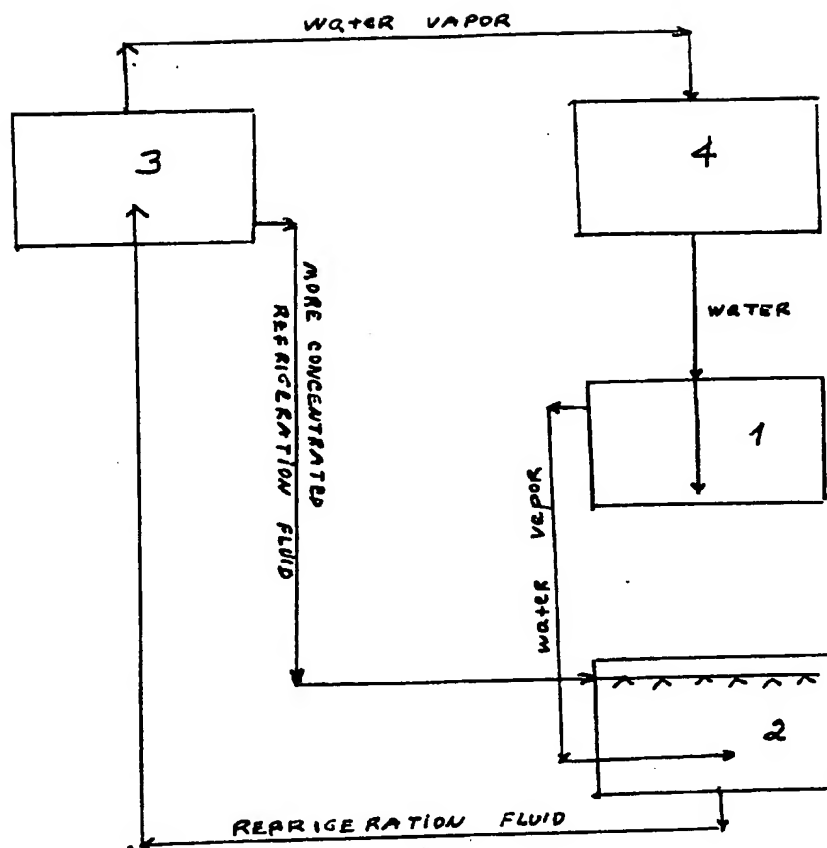
17. The method according to claim 16, wherein the fluorinated salt of lithium is lithium bis (trifluoro methane sulfonyl) imide.

18. The method according to claim 14, wherein the first phase represents a major portion of the refrigeration liquid.

19. The method according to Claim 14, wherein the refrigeration fluid further comprises  $\text{ZnBr}_2$ .

20. In an absorption refrigeration apparatus, the improvement which comprises a refrigeration fluid comprising a two-phase liquid wherein the first phase is an aqueous solution of a lithium halide, and the second phase is an aqueous solution of a fluorinated salt of lithium.

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**FIGURE 1**



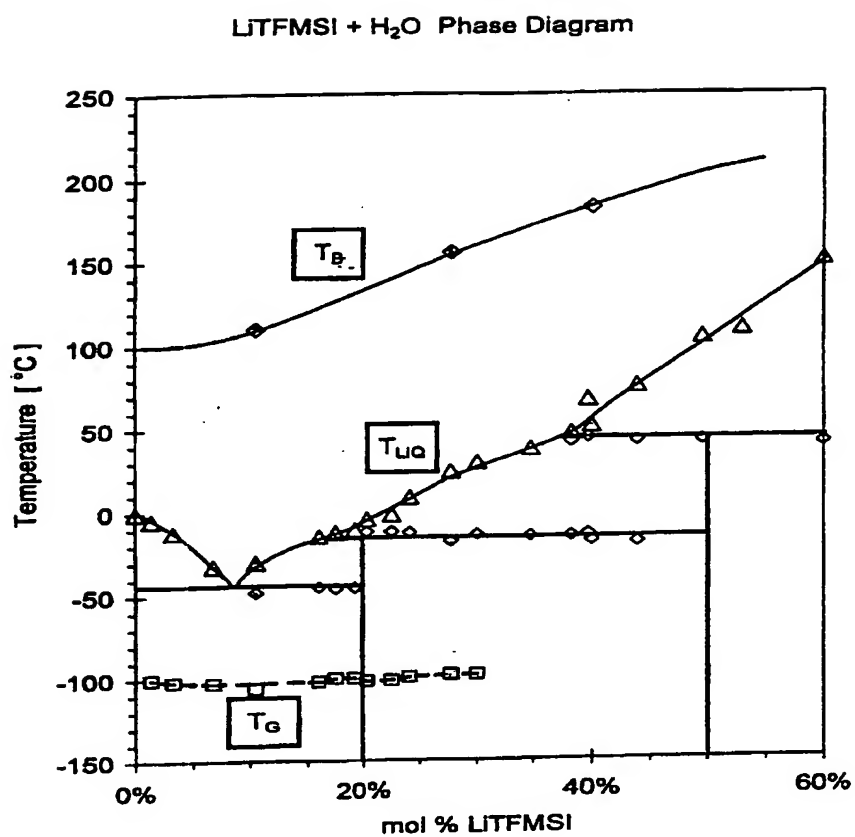
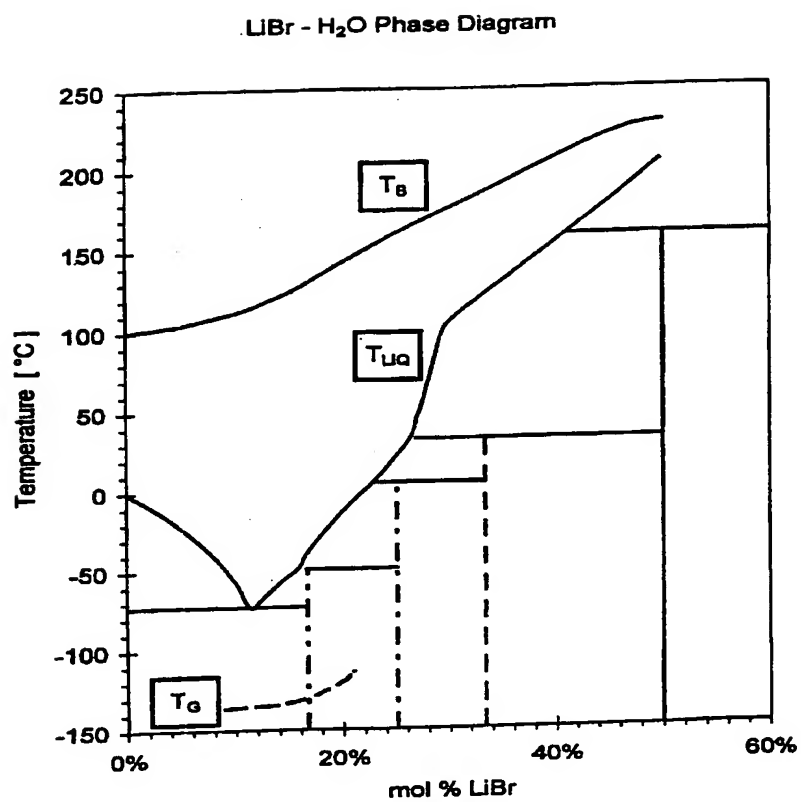
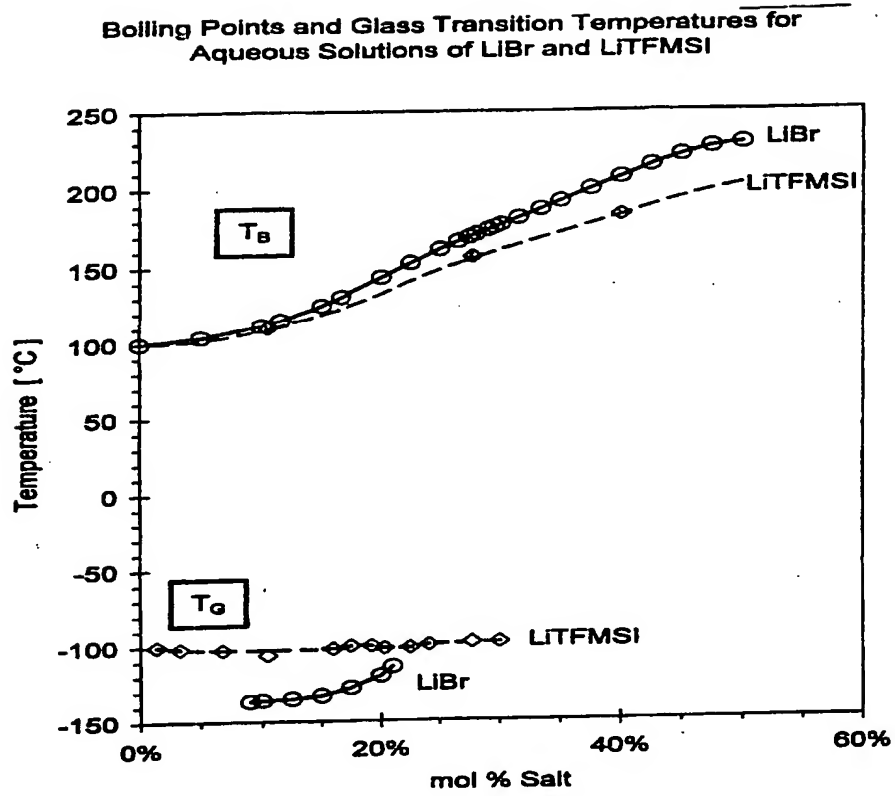


FIGURE 2

**FIGURE 3**

**FIGURE 4**

# INTERNATIONAL SEARCH REPORT

In International Application No  
PCT/US 00/09796

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09K5/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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EPO-Internal, WPI Data, PAJ, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 5 723 058 A (SCHUURMAN EIKO A) 3 March 1998 (1998-03-03) figure 1; examples II,III	1,7
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

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